CHAPTER II

PHYSICAL AND CHEMICAL CHARACTERISTICS OF THE WASTE CONSTITUENTS (40 CFR 264.94(b)(1)(i) and (2)(i))

The first step in any ACL demonstration is to identify the chemicals of concern. These "hazardous constituents" are chemicals listed in Appendix VIII of Part 261 of the regulations that have been detected in the ground water and may reasonably be expected to be related to the hazardous waste facility. The applicant must also account for the degradation products of all ACL constituents, especially if those products have significant toxicological properties. Once the hazardous constituents are identified, an ACL demonstration based on attenuation arguments must determine the physical and chemical characteristics of the constituents in order to effectively determine their transport through the environment and their ultimate fate. This chapter discusses the data that is needed to adequately characterize the physical and chemical properties of the hazardous constituents.

The permit applicant should already know which hazardous constituents are present in the ground water at the facility by the time an ACL demonstration is being considered. The §270.14(c) permitting requirements specify that the permit applicant must determine the extent of ground-water contamination when a significant increase in a ground-water contaminant occurs at the compliance point. Additional ground-water sample collection and analysis is usually not necessary for ACL purposes.

The hazardous constituents of concern during the permitting process can be any of the 375 contaminants listed in 40 CFR Part 261, Appendix VIII. The Agency does not require sampling for Appendix VIII substances that are unstable in ground water or for which no EPA-approved analytical method exists (U.S. EPA, l984b). The permit applicant should be aware that the Agency has proposed changing Appendix VIII monitoring requirements for ground water (July 24, 1986; 51 FR 26632). When this proposal is finalized (expected in June 1987), the Agency will use this list along with any site-specific additions to the list made by the Regional Administrator as the basis for detection and compliance monitoring programs.

Currently, an Appendix VIII analysis is required whenever any leakage from a facility's unit is detected by §§264.98 and 270.14(c)(4) monitoring. Assuring the absence of particular hazardous constituents emanating from a regulated unit is difficult to do simply by record-keeping. Wastes other than those that are currently received might have been placed in the unit in pre-record-keeping times. In addition, the potential exists for unpredicted reactions between the constituents and the formation of degradation products.

The fulfillment of the §270.l4(c) permitting requirements should result in the spatial characterization of each hazardous constituent found at the site. The permit applicant should submit, as part of the ACL demonstration, the data gathered to satisfy these requirements and present the information in terms of three-dimensional representations of constituent concentrations. The three- dimensional representation of ground-water contamination may not necessitate three-dimensional modeling of the contaminant plume. A two-dimensional model in the vertical and longitudinal planes may be sufficient in many cases, if the site hydrogeology is fairly homogeneous, and if sufficient monitoring data exists to describe the plume. See Chapter IV for further discussion of appropriate models.

The permit applicant should also submit, as part of the ACL demonstration, information on the chemical and physical characteristics of the wastes in the regulated unit that was gathered pursuant to §264.13. This data will give the ACL reviewer a better understanding of what may be expected to show up in the ground water. Additional waste constituent analyses may not be needed for the ACL demonstration if the applicant has fulfilled the requirements of §264.13.

Several physical and chemical characteristics of hazardous constituents are critical to the modeling of contaminant transport in ground water. Permit applicants should submit data on the following characteristics of the constituents for which ACLs based on fate and transport are requested: density, solubility, vapor pressure, viscosity, valence state, and octanol-water partitioning coefficient. For example, consider a facility that is leaking a hazardous constituent at a concentration level near or above the constituent's solubility level. In this case, there is a good possibility that a two-phase plume could result. One phase would be the dissolved constituent plume in the ground water, and the other would consist of relatively pure hazardous constituent. This latter phase could either be floating on the water table or sinking to an aquitard, depending on its density. The two phases would probably move at different rates due to viscosity and density differences.

Even when only one phase is present, the transport model results are dependent on the physical and chemical characteristics of the constituents; attenuation parameters for transport models depend on specific characteristics of the hazardous constituents. The permit applicant should submit in tabular form the density, solubility, vapor pressure, viscosity, and octanol-water partitioning coefficient values of the hazardous constituents. The ability for one constituent to mobilize other constituents should also be investigated. Appendix C contains an example of a summary sheet that can be used to list the important properties of the ACL constituents.

An ACL demonstration that is based on attenuation should be supported by data on fate-related characteristics of the ACL constituents. If a permit applicant argues that the presence of an ACL constituent at the point of compliance is not likely to cause exposure because it is not persistent in the ground water, then special fate and stability related characteristics of the constituent should be discussed in the ACL demonstration.

The stability of waste constituents in the subsurface environment can be affected by chemical, biological, and physical processes. Important chemically mediated subsurface processes may involve oxidation, reduction, and hydrolysis. Important biologically mediated processes include biodegradation and biotransformation reactions. The subsurface physically mediated processes can involve ion exchange, precipitation, and complexation reactions. If the ACL demonstration is based on any of these processes, then the results of site-specific tests should be submitted. Most of the degradation processes depend on the properties of contaminants as well as environmental factors such as microbial populations, solid surfaces, and dissolved constituents present in the ground water. Because the relevant environmental factors are unevenly distributed in nature, degradation and reaction rates are not constant in ground-water environments and must be assessed on a site-specific basis. Therefore, the use of general information gathered from the literature will be of limited value when assessing the stability of waste constituents.

Degradation properties of the ACL constituents are also important in determining the effects of the constituents. Since degradation products can be more hazardous than the parent compound, all known and likely degradation products should be discussed when describing the characteristics of the waste constituents.

Grouping ground-water contaminants according to stability characteristics may be possible. If site-specific tests support the grouping of constituents, then the fate and mobility of each constituent within a group can be based on the stability characteristics of the most mobile and most persistent compounds in the group. This would result in the fate and mobility coefficients for each constituent being set at the coefficient values for the most mobile and most stable compounds in the group. Before grouping the constituents, the applicant should investigate possible degradation products associated with the constituents of concern. The ability of one contaminant to facilitate or hinder the movement of another contaminant (co-solvent effects) should also be accounted for when possible. Although it is difficult to decide which groupings of constituents are appropriate, grouping can reduce the amount of predictive modeling necessary for quantifying environmental concentrations and exposure pathways (see U.S. EPA 1986c).

CHAPTER III

HYDROGEOLOGIC CHARACTERISTICS
(40 CFR 264.94(b)(1)(ii) and (2)(ii))

A general description of the hydrogeological characteristics of the facility is needed in all ACL demonstrations. A more detailed assessment of ground-water movement near a facility is essential to a demonstration based on attenuation. The main route of exposure to ground-water contaminants usually involves the movement of the hazardous constituents through the soil to the ground water and on to an existing or potential point of use. This chapter describes the information needed to adequately determine the hydrogeologic properties required for characterizing ground-water movement at a site.

During the general RCRA permitting process, the permit applicant is required under §270.14(c) to identify the uppermost aquifer. The uppermost aquifer is defined under §260.10 as the geologic formation nearest the natural ground surface that is an aquifer as well as lower aquifers that are hydraulically interconnected with this aquifer within the facility's property boundary. Saturated zones above the uppermost aquifer are also of interest as contaminant migration pathways. Therefore, for an ACL demonstration based on attenuation, information on the geologic and hydrologic properties of each of the individual strata beneath a facility, that are likely to influence ground-water contaminant migration, should be submitted. This data is needed to adequately characterize ground-water transport mechanisms. Much of the data should already be available to the permit applicant if the Section 270.14(c) requirements have been fulfilled.

The important geologic attributes of a facility include:

1. Soil and rock characteristics,
2. Geologic structure, and
3. Geomorphology and topography.

When describing the soil characteristics of a facility, the permit applicant should use the Unified Soil Classification System or the U.S. Department of Agriculture's soil classification system. Each soil type beneath the site and within the areal extent of the ground-water contaminant plume should be investigated. The permit applicant should submit data describing the thickness, areal extent, and hydraulic properties of each soil type. The soil information should be submitted in both tabular and graphic form. The areal extent of soil types should be presented on a map with a scale no greater than one inch:200 feet. The applicant should submit copies of drilling and boring logs from monitoring and water wells that have been installed.

If the applicant uses soil or other matrix attenuation mechanisms to justify the ACL, the additional data and calculations used to define the attenuative properties should be submitted. The following attenuation mechanisms may be relevant to an ACL demonstration:

1. Dispersion, including hydrodynamic dispersion;
2. Retardation, including all sorptive properties; and
3. Degradation, including mechanisms of biodegradation, oxidation, reduction, and hydrolysis.

The permit applicant should submit data describing the organic and mineral content, the cation and anion exchange capacity, and the grain size of each soil type in the area of contamination. Aquifer matrix characteristics that affect the stability of the ACL constituents (see Chapter II) should also be described if they are used to support attenuation claims. The results of tests to substantiate any attenuation claims should be submitted by the applicant. Likewise, sampling and laboratory procedures used to determine the attenuation properties should be presented and results tabulated. Brady (1974) and Freeze and Cherry (1979) provide in-depth discussions of these specific soil characteristics, and the permit applicant and reviewer should consult these references for assistance.

The permitting authority and the applicant should keep in mind the outcome of the different types of attenuation. Although matrix effects (binding) and dispersion act to lower the concentration of the contaminants at the point of exposure, they do not directly reduce their total mass. Constituents that attach to the matrix may become mobilized at a later time. However, degradation mechanisms act to eliminate the contaminants themselves. This form of attenuation is permanent and, assuming the products are harmless, can be a final solution to eliminating the contamination.

If the ACL demonstration is attenuation-based, the permit applicant should submit a set of maps that adequately depict the subsurface stratigraphy. The near-surface stratigraphic units in the zone of saturation that affect or are likely to affect ground-water contaminant migration should be described. The areal and vertical extent of the hydrogeologic units can be presented in several ways. For complex settings, the most desirable presentation is a series of structural contour maps for the top or bottom of each unit. Vertical sections and isopach maps can also be used since they are generally more graphic and are useful as supplements to the structural contour maps. Because the construction of any of these diagrams involves interpolation and extrapolation of data, the diagrams should show the location of control points and the corresponding value at each control point. The site maps should include the depth, thickness, and areal extent of each stratigraphic unit. The maps should also adequately depict all stratigraphic zones and lenses within the near-surface zone of saturation. The site-specific stratigraphic maps should be detailed and have a scale no greater than one inch:200 feet. The applicant should also submit regional stratigraphy maps in order to show unique regional characteristics and their relationships to the site and to justify claims concerning the ultimate fate of a contaminant plume. A table that summarizes the subsurface geologic data should be submitted.

Each of the stratigraphic units located in the zone of saturation should be characterized for the hydrologic parameters of hydraulic conductivity (vertical and horizontal), specific yield (unconfined aquifer) or specific storage (confined aquifer), and effective porosity. Hydraulic conductivity and porosity of aquifer material can be determined by using laboratory or field methods. It is recommended that all tests that are conducted to define the hydraulic properties of each stratigraphic unit be performed in the field. Laboratory tests may be used to substantiate field test results but should not be the sole basis for determining aquifer characteristics. Only in special cases will the submittal of laboratory analyses be considered adequate for describing aquifer characteristics. Literature value estimates for these parameters will rarely be acceptable.

Each of the hydrologic parameters can vary from point to point, even within the same aquifer. Therefore, the areal variations of the parameters within the stratigraphic units should be characterized. The amount of data necessary to characterize a stratigraphic unit will increase with the increasing heterogeneity of the unit. As an example, an aquifer of extensive homogeneous beach sand will require less investigation than a glacial unit consisting of lenticular deposits of outwash sand and gravel interbedded with clayey till. However, in order to save time and effort, the applicant may choose to make simplified "worst case" assumptions of hydraulic conductivity and porosity.

There are many field methods for measuring hydraulic conductivity and porosity. Hydraulic conductivity is most effectively determined from the analysis of pump test data. For units having low hydrologic conductivity, single-well tests are generally used (i.e., a slug test). For units having high hydraulic conductivity, multi-well pumping tests are necessary. The pump test methods are normally designed to evaluate the transmissivity and storativity (storage coefficient) of the aquifer. Hydraulic conductivity is determined by dividing transmissivity by the aquifer thickness. More information on determining aquifer characteristics can be found in Freeze and Cherry (1979), Kruseman and De Ridder (1979), U.S. EPA (l983a), and Walton (1970).

Different laboratory methods can be used to substantiate field data. Hydraulic conductivity may be determined on a core sample of the aquifer by using either a constant-head or a falling-head permeameter. A description of the method can be found in Todd (1980) and Bouwer (1978). In the laboratory, effective porosity can be determined as the ratio of the volume of water yielded by gravity flow to the volume of soil or rock material.

If an aquitard separates two distinct ground-water zones, then the physical and hydraulic characteristics of that aquitard must be provided in sufficient detail to illustrate the degree of interconnection between the two aquifers. This requirement can be fulfilled by providing the results of an aquifer pump test designed to show the effect of the pumping of the deeper aquifer on the shallow aquifer. The shallow aquifer will exhibit significant drawdown during the pump test if the two aquifers are interconnected.

A summary of the hydraulic properties of each stratigraphic zone within the zone of saturation should be submitted by the permit applicant. This data should be provided in a table that includes the aquifer name, stratigraphic zone, vertical conductivity, horizontal conductivity, specific yield, transmissivity, and storage coefficient.

CHAPTER IV

GROUND-WATER FLOW DIRECTION AND QUANTITY (40 CFR 264.94(b)(1)(iii) and (2)(iii))

The amount or quantity of ground water at a site and the direction in which it flows are two essential components of an analysis of the fate and transport of hazardous constituents in the ground water. The ultimate fate of contaminated ground water is a principal topic of every attenuation-based ACL demonstration since a contaminant plume may discharge into and mix with other ground or surface waters. This chapter describes methods that can be used to determine ground-water flow direction and quantity at a site. The EPA publication Ground-Water Monitoring Technical Enforcement Guidance Document (U.S. EPA 1986a) may also be useful in making these determinations. However, if a facility is located over a relatively complex hydrogeologic system (e.g., fractured rock or karst aquifers), setting the POE at the POC may be the only acceptable method for establishing the ACL.

The primary processes that control the migration of contaminants in subsurface environments include:

1. Advection (movement of the ground water),
2. Hydrodynamic dispersion (mixing of ground water having different levels of contamination), and
3. Chemical reactions.

For ACL purposes, advection is defined as the migration of hazardous constituents by actual motion or flow and is generally assumed to be caused by natural ground- water flow. Consideration of advection alone presents the worst-case calculations in terms of peak arrival times and concentration strengths. Furthermore, qualitative and quantitative evaluation of advection in terms of flow pathways is possible.

The Section 270.14(c) permit requirements specify the submittal of ground-water flow information. This data should be adequate for on-site determinations of flow; however, additional data may be required if off-site determinations of ground- water flow are needed for the ACL demonstration. The permit applicant should evaluate ground-water flow in terms of the flow regime present at the facility. Flow from the facility to the water table will generally occur in the unsaturated zone, although it may go via surface water. Where subsurface heterogeneities are not significant, it is reasonable to assume that flow through the unsaturated zone will be predominantly downward. This assumption is justified because gravity is the primary force acting on a fluid in the unsaturated zone.

Once in the saturated zone, dissolved constituents will move with the ground water. Evaluation of advective transport in the saturated zone for miscible constituents can generally be based on the observed ground-water flow field and hydraulic properties (hydraulic conductivity gradient and effective porosity). The observed flow field can be determined by a combination of areal water level maps and vertical sections showing water levels.

Calculations of ground-water quantity will require the use of the subsurface hydrogeologic parameters described in Chapter III. Ground-water quantity can be estimated by calculating the porosity of the aquifer. The use of Darcy's law for determining ground-water flow quantity is acceptable and can be found in any standard ground-water textbook (e.g., Freeze and Cherry (1979)). Darcy's law can be used to calculate specific discharge or volume rate of flow through a cross-sectional area perpendicular to the flow direction in relatively homogenous systems.

The determination of ground-water flow rates and directions is simple in concept. If the distribution of hydraulic head and the hydrologic properties at the site are known, then a flow net or water level contour map in conjunction with the use of Darcy's law can be used to determine flow rates and directions.

The permit applicant should be aware of a number of factors that can make accurate determination of ground-water flow difficult. These include:

1. Low horizontal or relatively flat gradients,
2. High vertical or relatively steep gradients,

3. Temporal variations in water levels,
4. Heterogeneous properties, and
5. Anisotropic properties.

In areas of low horizontal gradients, small errors in water level measurements or small transient changes in water levels can make determination of flow direction and rates difficult. High vertical gradients often exist in surficial units. In recharge areas, head decreases with depth; whereas in discharge areas, it increases with depth. Often, a shallow water table aquifer may overlie an aquifer of higher permeability, resulting in vertical head gradients. A very common mistake is made when water level contour maps are constructed using wells or piezometers at different depths. In such a case, calculated horizontal flow directions may be inaccurate.

Water levels can vary temporally because of short-term stresses, tidal effects, atmospheric pressure variations, seasonal effects, and long-term trends. In determining flow direction, the annually averaged water levels are of primary interest. Consideration of short-term effects is more important at sites with low hydraulic gradients. In evaluating any water level data, the uncertainty introduced by neglecting short-term effects must be estimated. Seasonal variations in recharge can result in significant water level variations in unconfined aquifers. Artificial recharge and certain types of ground-water pumpage often lead to seasonal changes in water levels. These changes may occur under both confined and unconfined conditions.

The degree of heterogeneity in aquifers may range from fairly moderate to extreme. The potentiometric surfaces or water levels in heterogeneous aquifers are not smooth regular surfaces. At the contact between two geologic materials, the hydraulic gradient will be discontinuous. For some aquifers, such as fractured rock and karst aquifers, the heterogeneity is much more complex.

Another property of an aquifer is its anisotropy. Hydraulic conductivity is a property that is dependent on direction and therefore has three principal components. If the principal components are equal, then the aquifer is isotropic. If not, the aquifer is anisotropic. For anisotropic aquifers, flow lines are not perpendicular to equipotential lines or water levels. Many aquifers display a horizontal-vertical anisotropy. However, if the two horizontal components of hydraulic conductivity are equal, then, from an areal perspective, flow lines will be perpendicular to lines of equal potential. Aquifers that may demonstrate horizontal anisotropy include aquifers in fluvial sandstone, fractured rocks, or steeply inclined strata. Ground-water flow direction is difficult to determine from water level data in these types of anisotrophic aquifers.

The factors that make the determination of flow rates and directions unreliable can often be overcome by an expanded effort in water level monitoring. For seasonal variations in water levels, a higher frequency monitoring schedule is necessary. For low horizontal gradients, the effects of short-term changes in water levels can be analyzed by installation of continuous recorders in selected wells. In aquifers having significant vertical gradients, piezometers completed at various depths may be required in order to provide a three-dimensional description of the flow field. For heterogeneous and anisotropic aquifers, more water level monitoring wells and more field tests for hydraulic properties are required.

The hydrogeologic portion of the ACL demonstration must include an adequate description of both horizontal and vertical ground-water flow components. This is required because it will help determine where the hazardous constituents may migrate. The horizontal ground-water flow description should include a flow net based on ground-water elevation measurements taken from monitoring wells or piezometers screened at the same elevation in the same saturated zone. The monitoring system must be designed to provide reliable results of the ground-water flow direction in the zone of saturation. There may be sites that will require the applicant to monitor for hazardous constituents at more than one ground-water elevation. When this situation occurs, the permit applicant must be especially careful to ensure that the monitoring plan is designed correctly.

Information obtained from analyses of the hydrogeological properties and flow direction will allow the calculation of ground-water flow velocity. Well identifier codes, well depths, screened intervals, ground-water elevations, and sampling data should be presented in tabular form. The flow net data should be graphically portrayed on a site map that includes ground-water elevations, isopleths, and flow vectors. As discussed before, the ground-water flow velocity can be determined by a simple modification of Darcy's equation if the aquifer is relatively isotropic. All calculations and assumptions should be included in the discussion of flow rates.

Vertical ground-water gradients and flow should also be described. Facilities should have several nested piezometers for vertical gradient determinations. Vertical flow gradient will aid in determining discharge and recharge zones, aquitard characteristics, and whether the monitoring wells are located and screened at the appropriate depths. The data that should be submitted in tabular form for each well nest includes well identification code, well depth, screened interval, ground-water elevation, and sampling date. All calculations and assumptions should be described in detail.

Facilities that are located in environmental settings that exhibit temporal variation in ground-water flow direction should define the extent to which the flow change occurs. The main causes of ground-water flow variation are:

1. Seasonality of recharge or discharge,
2. Ground-water withdrawals,
3. Underground injection,
4. Surface water elevation changes, and
5. Artificially induced recharge by basin flooding.

In cases of seasonal ground-water flow variation, the permit applicant should provide information describing those temporal changes in ground-water flow direction using records compiled over a period of no less than one year.

The rate of withdrawal of ground water is an important factor that influences ground-water and contaminant movement and exposure to contaminated water. In attenuation-based demonstrations, the rate of ground-water withdrawal in the vicinity (5 km radius) of the facility should be summarized in tabular form and should include well location, depth, type of use, and withdrawal rates. The zone of impact created by any major well or well field withdrawal should be identified on a site map. The map should include drawdown isolines out to the 30 centimeter drawdown level. Modeling of drawdown curves should use low recharge assumptions such as drought conditions.

Models

Although not required for an ACL demonstration, mathematical simulation models of ground-water flow and contaminant transport can be extremely useful tools for the applicant. Models are more appropriate for relatively simple geologic environments where conditions do not vary widely; in complex geologic areas, modeling may be less useful.

The permit applicant is responsible for ensuring that the models used simulate as precisely as possible the characteristics of the site and the contaminants and minimize the estimates and assumptions required. All models used in the demonstration should:

1. Be compatible with the quality and type of input data available,
2. Have been demonstrated to be applicable to the environmental conditions at the site,
3. Have been subjected to an independent quality assurance audit or to a level of professional peer review equivalent to that for publication in a scientific or technical journal,
4. Be internally consistent in the use of boundary and initial conditions, time steps, assumptions, and code modifications,
5. Have fully documented support available to the Agency, and
6. Be calibrated and verified for the site before being applied in a predictive mode.

As discussed in Chapter II, a two-dimensional model of a ground-water system may be used; however, all simplifying assumptions must be justified. Whenever possible, input parameters and assumptions should be conservative in nature; worst-case scenarios may save much effort. If models are used, the ACL demonstration should include tables of the assumptions, the input parameters, and any calibration data.